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Description

The invention relates to a nickel-based catalyst, to its preparation and to its application for hydrogenation reactions.

Nickel-based catalysts are well-known and are widely used as hydrogenation catalysts. It is customary to prepere them by precipitating nickel-hydroxide and/or -carbonate from an aqueous solution of a nickel salt using en alkaline reectent, often in the presence of e carrier.

In the preparation of these catalysts measures are often taken to precipitete the insoluble nickel compounds as gradually as possible from the solution onto the carrier particles suspended therein. To this end, for example, a carrier suspension in a solution of a nickel-ammonia complex is heated so as to allow the ammonia to escape, thereby causing the nickel to precipitate (cf. GB-A-926 235). Alternatively, urea is incorporated in the solution in which the carrier is suspended, after which the urea is decomposed by heating (cf. GB-A-1 220 105), causing the nickel hydroxide to precipitate. The aim of this very gradual precipitation of the nickel is to cover the carrier particles entirely or largely with nickel compound. Furthermore, GB-A-1 367 088 discloses the preparation of a catalyst by precipitating nickel on guhr, keeping temperature, pH, alkalinity and residence time within narrow ranges. In this process tho nickel hydroxide is slowly precipitated from a diluted solution in a reaction vessel, after which the solid components are separated. Precipitation and post-reaction (the latter normally being referred to as "ageing") take place in the same reaction vessel, which therefore has to be relatively big, under the same reaction conditions.

It has now been found however that new, improved nickel-based catalysts as defined in claim 1 can be prepared by carrying out this process in at least two separate steps, to wit: (i) A very rapid precipitation step, in which under vigorous agitation the nickel hydroxide/carbonate is precipitated in e precipitetion reector with a mean residence time of 0.01 to 10, preferably 0.2 to 4.5 minutes, rather even less than 3.5 minutes, during which the normality of the solution in the reactor, containing excess alkali, is between 0.05 and 0.5, preferably between 0.1 and 0.3 N and the temperature of the liquid in the precipitation reactor is kept between 5 and 95°, preferably between 20 and 55°C. (ii) At least one separate, longer ageing step with a mean residence time in the post-reactor of 20 to 180 min, and a temperature that remains between 60 and 100°, preferably between 90 and 98°C. It is sometimes preferred for the temperature during the ageing step(s) to differ from that during the precipitation step; in particular it may be advantageous to perform the ageing step at somewhat higher temperatures, e.g. with a difference of 10°C above the precipitation temperature.

The nickel-based catalysts according to the present invention comprise a water-insoluble carrier material which is present or added during preparation. Suitable carrier materials are for example silica-containing materials such as kieselguhr, aluminium trioxide, and silicates such as bentonite. Kieselguhr is the preferred material, particularly kieselguhr containing from 50 to 90 wt.% of amorphous silica.

The carrier material can be added (a) directly as such, (b) as an aqueous suspension, (c) preferably as a suspension in an aqueous nickel salt solution, (d) as a suspension in an aqueous solution of the alkaline compound.

According to embodiments (a) - (d) the carrier can be added before or during precipitation. According to embodiments (a), (b) or (d), however, the carrier can also be added entirely or partly (the latter being preferred) after precipitation, but also before or during ageing.

After precipitation and ageing according to the invention the solids are separated from the liquid, optionally washed, dried and activated by contacting them with hydrogen at an elevated temperature in a manner known per se.

Nickel compounds which can be used as starting materials for the preparation of the catalysts according to the present invention are water-soluble nickel compounds such as nitrate, sulphate, acetate and chloride. The solutions that are fed into the precipitation reactor preferably contain between 10 and 80 g nickel per litre; particularly preferred is the use of solutions containing between 25 and 60 g nickel per litre.

Alkaline compounds which can be used as starting material in the process according to the present invention are alkalimetal hydroxides, alkalimetal carbonate, alkalimetal bicarbonate, the corresponding ammonium compounds and mixtures of the above-mentioned compounds. The concentration of the alkaline solution fed into the precipitation reactor is preferably 20-300 g of anhydrous material per litre (as far as the solubility permits this), particularly between 50 and 250 g per litre.

It has practical advantages to use the two solutions (nickel-containing and alkaline, respectively) in ebout equal concentrations expressed in equivalents, resulting in the use of about equal volumes.

The nickel-containing solution and the alkaline solution are fed at such rates that a slight excess of alkaline compound is present during the precipitation step, namely such that the normality of the liquid ranges from 0.05 to 0.5, preferably from 0.1 to 0,3 (said normality being determined by titration with aqueous hydrochloric acid using methylorange as the indicator). In the ageing step it may sometimes be desirable to add further alkaline solution in order to maintain the alkalinity (normality) in the abovedefined range.

Th pr cipitation reactor comprises a means for vigorous agitation of the reacting fluid and its dimensi ns are such in relation to the amounts of fluid fed that the short m an residence times indicated can be obtained. Preferred mean residence times in the precipitation reactor are normally b tween 0.01 and 10, particularly between 0.2 and 4.5 minutes. The precipitation step and also the ageing step can be carried out batchwise, continuously and semi-continuously (e.g. according to the cascade method).

In th preferred continuous precipitation process (step i) the rate f addition of the solutions t th

precipitation reactor is controlled by continuously or discontinuously measuring the alkalinity (normality) of the discharged liquid. This can sometimes also be done by monitoring the pH. Also the temperatures of the reacting liquids fed into the precipitation reactor are used to control the temperature at which precipitation takes place. The required vigorous agitation of the liquid in the precipitation reactor preferably takes place with an energy input of 5-25 K watts per 1000 kg of solution. Jet mixing is also a suitable method, involving much larger specific energy inputs of up to 2000 watts/kg.

The reaction mixture obtained from the precipitation reactor is subsequently led into a significantly larger post-reactor, in which the liquid is further agitated. If desired, additional ingredients can be incorporated here, such as carrier material, alkaline solution as defined hereinbefore and/or possibly promoters.

Preferably the temperature of the liquid in the postreactor, i.e. during the ageing step, is kept at a temperature between 60 and 100°C, preferably between 90 and 98°C.

The normality of the liquid in the post-reactor during the ageing step (step ii) is kept in the same range as during the precipitation step (step i); it may be required to add some further alkali. The ageing step can be performed in one or more post-reactors, the (overall) mean residence time being kept between 20 and 180 min, preferably between 60 and 150 min. If two or more postreactors are used it is desirable to arrange this in such a way that in the second or following post-reactor the temperature of the liquid is 10 to 15 centrigrades below the temperature in the first post-reactor.

After completion of the ageing step the solids are separated from the mother liquor, usually washed, dried, optionally ground and/or calcinated and subsequently activated with hydrogen gas at an elevated temperature usually ranging between 250 and 500°, preferably between 300 and 400°C. This activation can take place at atmospheric or higher pressure. Atmospheric pressure is preferred.

Preferably before drying, or during any previous step promoters can conveniently be added. Promoters comprise emounts of 0.05 to 10%, calculated on the weight of nickel, of metals/compounds such as copper, cobalt, zirconium, molybdenum, silver, magnesium, eny other metals and combinations thereof.

The separated solid is preferably washed with water, sometimes made slightly alkaline, or water with a detergent added thereto.

Organic solvents can sometimes be used advantageously. Drying takes place preferably with forced air circulation. Spray-drying end freeze-drying are also quite well possible.

The present invention provides new, improved nickelbased catalysts which comprise 10-90 parts by weight of nickel/nickel compounds and 90-10 parts by weight of a water -insoluble carrier material, as well as 0-10, preferably 0.05-5-parts by weight of a metal promoter, which catalysts have an active nickel surface of 70-200 m^2/g, preferably more than 100 m^2/g, said cetalysts further comprising aggregates which mainly consist of nickel/ nickel compounds with an average particle size of 2 to 100 micrometers µm, preferably between 5 and 25 micrometers µm, and which aggregates have an (outer) surface which is for at least 60% free of carrier perticles attached thereto. Preferably the nickel/nickel compound aggregates have a surface which is for more than 80%, particularly for more than 90% free of carrier particles.

The nickel-based cetalyst, comprising an insoluble carrier and optionally a promotor can be prepared by a process involving precipitation of nickelhydroxide/carbonate, ageing,separation and reduction characterized in that there are at least two steps to wit (I) a rapid precipitation step, in which under vigorous agitation the nickel hydroxide/carbonate is precipitated in a precipitation reactor with a mean residence time of 0.01 to 10, preferably 0.2 to 4.5 minutes, during which the normality of the solution in the reactor, containing excess alkali, is between 0.05 end 0.5, preferably between 0.1 and 0.3 N and the temperature of the liquid in the precipitation reactor is kept between 5 and 95°, preferably between 20 and 55°C followed by (II) at least one separate, longer ageing step with a mean residence time in the post-reactor of 20 to 180 min., preferably between 60 and 100°, preferably between 90 and 98°C, after which the solid is separated, dried and reduced with hydrogen in a manner known per se.

The nickel/nickel compound aggregates consist mainly, i.e. for more than 80%, preferably more than 90%, of nickel and nickel oxides, but some promoter material may also be present. These aggregates preferably contain nickel crystallites with an average diameter between 0.5 and 10, more particularly between 1 and 3 nanometers ηm.

The catalyst according to the invention is used for the hydrogenation of unsaturated organic compounds, in particular oils and fats, fatty acid and derivatives thereof.

The invention is illustrated by the following Examples.

Example 1

An aqueous suspension was prepared by suspending kieselguhr (containing 7.0% amorphous SiO_2) in a $NiSO_4$ solution (35 g Ni/l and 1.2 N), in such a way that the Ni:SiO_2-ratio was 1:2.3. Also an aqueous soda s lution, containing 75 g of Na_2CO_3 (enh) per litre and 1.4 N, was prepared. Subsequently b th solutions were continuously pumped int a vigorously agitated pump reactor, in about equal volumes, resulting in precipitation of nickelhydroxide/carbonat at a temperature of 80°C. The alkalinity of the suspension so obtained was 0.096 N. In the reactor in which the precipitation took place the suspension had a residence time of 4 minut s, after which the suspension was immediately passed to the first of a series of two postreactors. In each of these post-reactors

the precipitate was aged for 50 minutes (mean residence time) at temperatures of 97° and 80°C, respectively. The aged precipitate was then continuously filtered off and the green filter cake thus obtained was washed with water, dried and activated with hydrogen under atmospheric pressure at a temperature of 350°C.

Electron microscopy and microröntgen analysis showed that the catalyst consisted of nickel crystallites averaging 2 nanom ters (ηm) and aggregates averaging 21 micrometers (μ). The surface of the nickel/nickel compound aggregates was for about 85% free of carrier particles and also the original shape of the siliceous skeletons was largely uncovered and well and freely perceptible.

Examples 2-7

Following the procedure as described in Example 1 further catalysts were prepared according to the invention, while varying the amounts and conditions, as is shown in Table I. Measures were taken to keep the other conditions unchanged.

In Table II, showing the hydrogenation characteristics of this catalyst, comparisons are made with a catalyst known from the literature.

On fatty acid hydrogenation it was found that for achieving a certain iodine value, with catalysts according to the invention less than half the hydrogenation time was sufficient and that in the case of fish oil the catalyst also retained its activity for a longer period. From the melting points it appeared that the new catalyst had a greater selectivity, i.e. less tri-saturated triglyceride was formed.

On fatty acid hydrogenation it turned out that hydrogenation could be carried through to lower iodine values in the same hydrogenation time and thus proceeded more rapidly than with the known catalyst used for comparison. Furthermore, the hydrogenations can also be performed with excellent results at a lower hydrogenation temperature. In addition, the new catalyst could be filtered very effectively, in any case better than the known catalyst.

Table III below gives an impression of fatty acid hydrogenation plotted against time (relation between iodine value and hydrogenation time under otherwise equal conditions).

TABLE III

Hydrogenation time (min)	Iodine value with catalyst 4 (Table II)	Iodine value with known catalyst (Table II)
30	45.1	72.1
60	15.3	45.5
90	9.8	22.2
120	5.3	17.8
150	3.3	15.1

Table III demonstrates that the iodine value of the hydrogenated fatty acid of about 15.2, obtained with the conventional catalyst widely used for this purpose after about 150 minutes, was already reached in about 60 minutes with the catalyst according to the invention, which is a considerable technological improvement.

TABLE I

Example:	1	2	3	4	5	6	7
$Ni:SiO_2$ ratio	2.3	2.3	2.3	2.3	2.3	1.8	1.8
Precipitation							
Conc. soda solution, mol/l	0.7	0.7	0.7	0.7	0.7	0.7	1.0
Conc. nickel solution, mol/l	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Precipitation temp. (°C)	80	20	30	55	50	85	22
Mean resid. time (step 1), min	4	1	1	1	1	0.3	0.5
Excess alkali (normality)	0.10	0.19	0.21	0.22	0.21	0.13	0.21
Ageing of precipitate							
Number of post-reactors	2	2	1	2	2	1	1
Temperature (°C)	97/80	97/80	96	93/80	90/77	95	97
Mean resid. time (step 2) in minutes	50/50	50/50	50	50/50	85/50	30	30
Excess alkali (mol/l)	0.135/ 0.192*	--	--	--	--	--	--
* = extra alkali							

Catalysts 1-5 contained 70% nickel and 30% SiO_2; catalysts 6 and 7 contained 64% nickel and 36% SiO_2.

Active nickel surfaces ranged between 120 and 150 m^2/g nickel.

Nickel aggregates were found to range between 9 and 26 micrometers (nm) and the catalyst of Example 4 was shown to have nickel aggregates the surface at which proved to be for 85% free of carrier particles.

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TABLE II

Example	1	2	3	4	5	6	7	Compar. example
Ni % in reduced catalyst	52.4	51.8	52.6	53.0	52.7	51.2	52.0	22 (in fat susp.)
Oil hydrogen. test refined marine oil of I.V. 165 to 85; conditi ns: 250 g oil, 0,1% Ni on oil, 60LH_2/h press, 1 bar, max. temp. 180°C, 750 rpm, reduct. temp. of cat. 350°C								
Hydrogen. time (min)	92	85	83	92	85	90	103	127
m.p. of oil (°C)	32	32.5	32	32.5	32.5	33	32.5	36
fatty acid hydrog. test 300 g tallow fatty acid (olein fraction) 0,07 Ni on fatty acid, H_2 press. 30 bar max. temp. 180°C Stirring speed 850 rpm hydrog. time 150 min reduction cat. 350°C								
I.V after hydr.	3.1	2.5	3.2	3.3	2.6	3.4	3.0	15.1

Example 8

A 10% aqueous soda solution and a 3.5% aqueous nickel sulphate (calculated as nickel) solution in which kieselguhr (22 g per litre) had been blended were both continuously pumped into a small precipitation reactor (75 ml capacity) whilst the reactor was heavily agitated (energy input 6 Watts per litre of solution). The two liquids were fed into the reactor in such rates that the pH in the precipitation reactor was 9.3. The residence time was 0.5 minutes.

After precipitation the slurry contained about 4% of solids and this slurry was continuously aged in a relatively larger vessel (capacity 4.5 l) with moderate stirring. The ageing temperature was 97°C and the pH was 8.9. The average residence time in the ageing reactor was about 30 minutes.

After 1.5 hours the flows were stopped and 4.5 l of slurry were filtered in a Büchner funnel under vacuum. After filtration the solids (filter cake) were washed with 4 litres of distilled water. The filter cake was then dried overnight in an oven at 120°C.

Samples of the green filter cake were investigated by electron microscopy (magnification 500 and 1000 x). The photos showed small nickel/nickel compound aggregates of which 80% were free of carrier particles and also the original shapes of the siliceous skeletons were largely uncovered by nickel/nickel compounds and freely perceptible.

The green cakes were reduced at 400°C with a hydrogen flow of 15 N (S:T:P) m^3/kg Ni for 30 minutes.

The active nickel surface area was determined by hydrogen chemisorption and yielded a value of 110 m^2/g nickel. The average size of the nickel crystallites was calculated to be 3 nanometers (ηm) and the size of the nickel/nickel compound aggregates was found to be 30 micrometers (μm).

This catalyst had excellent properties for the hydrogenation of soybean and fish oils.

Claims

1. Hydrogenation catalyst, containing 10-90 parts by weight of nickel/nickel compounds and 90-10 parts by weight of a water-insoluble carrier material and having an overall active nickel surface of 70-200 m^2/g, preferably more than 100 m^2/g per gram nickel, characterized in that the catalyst comprises nickel/nickel compound aggregates with an average particle size ranging from 2 to 100 micrometers (μm) and that the surface of the nickel/nickel compound aggregates are for at least 60% free of carrier particles.

2. Hydrogenation catalyst according to claim 1, characterized in that the surface of the nickel/nickel compound aggregates is for at least 80% free of carrier particles.

3. Hydrogenation catalyst according to claim 1 or 2, characterized in that the surface of the nickel/nickel compound aggregates are for at least 90% free of carrier particles.

4. Hydrogenation catalyst according to any one of claims 1-3, characterized in that the average particle size of tha nickel/nickal compound aggregates ranges between 5 and 25 micrometers (μm).

5. Hydrogenation catalyst according to any ona of claims 1-4, characterized in that the average nickel crystallite slza ranges between 0.5 and 10 nanometers (ηm).

6. Hydroganation catalyst according to any one of claims 1-5, characterized in that the nickel crystallite size ranges from 1 to 3 nanometers (ηm).

7. Process for preparing a nickel-based catalyst, comprising a water-insolubla carrier and optionally a promotor, according to claim 1, which process involves precipitation of nickelhydroxlde/carbonata ageing, separation and reduction, characterizad in that there are at least two staps to wit (I) a rapid precipitation step, in which undar vigorous agitation tha nickel hydroxlde/carbonate is pracipitated in a pracipitation reactor with a mean residenca time of 0.01 to 10, preferably 0.2 to 4.5 minutes, during which the normality of the solution in th reector, contalning excess alkall, is between 0.05 and 0.5, preferably betwean 0.1 and 0.3 N, and tha temperature of tha liquid in the precipitation raactor is kapt batween 5 and 95°, praferably between 20 and 55°C, followed by (II) at laast one separata, longar ageing stap with a mean rosidence time in the postreactor of 20 to 180 min., preferably between 60 end 100°, preferably between 90 and 98°C, after which the solid is separated, dried and reduced with hydrogen In a manner known per se.

8. Process according to claim 7, characterized in that the nickel salt solution to be precipitated contains 10-80 g nickel per litra.

9. Procass according to claims 7 or 8, characterized in that tha carrier is added in an amount of 20-200 g per litra.

10. Process according to any one of claims 7-9, charactarized in that the solution of the alkalina compound contains from 30 to 300 g of anhydrous alkalina compound par litra.

11. Process according to any one of claims 7-10, characterized in that the alkalina solution contains sodium carbonate.

12. Process according t any one of claims 7-11, characterized in that the nickal compound is a salt of a mineral acid.

13. Proc ss according to any of claims 7-12, characterized in that th carrler is silica.

14. Process according to claim 13, characterized in that the silica used is kieselguhr consisting for 50 to 90 wt.% of amorphous SiO_2.

15. Process according to any one of claims 7-14, characterized in that during precipitation agitation takes place with a mechanical energy input of 5-5000, preferably 5-25 kilowatts per 1000 litres of solution.

16. Process according to any one of claims 7-14, characterized in that mechanical agitation is effected by jet mixing.

17. Process according to any one of claims 7-16, characterized in that the activation of the catalyst is carried out with hydrogen at a temperature between 250 and 500°, preferably between 300 and 400°C.

18. Process according to any one of claims 7-17, characterized in that precipitation is carried out continuously by dosing a carrier suspension in an aqueous nickel salt solution together with an alkaline solution in a small, vigorously rotating mixing pump and subsequently pumping the suspension into one or more post-reactors.

19. Process according to claim 18, characterized in that two or more post-reactors are used, the temperature in the second and any following post-reactor being 5-15 °C lower than that in the first post-reactor.

20. Use of nickel catalysts as described in any of the preceding claims in the hydrogenation of unsaturated organic compounds.

Patentansprüche

1. Hydrierungskatalysator, der 10 bis 90 Gew.-Teile Nickel/Nickelverbindungen und 90 bis 10 Gew.-Teile eines wasserunlöslichen Trägermaterials enthält sowie eine gesamte aktive Nickeloberfläche von 70 bis 200 m^2/g, vorzugsweise mehr als 100 m^2/g, pro Gramm Nickel aufweist, dadurch gekennzeichnet, daß der Katalysator Nickel/Nickelverbindung-Aggregate mit einer durchschnittlichen Teilchengröße im Bereich von 2 bis 100µm enthält, und daß die Oberfläche der Nickel/Nickelverbindung-Aggregate zu mindestens 60 % frei von Trägerteilchen ist.

2. Hydrierungskatalysator gemäß Anspruch 1, dadurch gekennzeichnet, daß die Oberfläche der Nickel/Nickelverbindung-Aggregate zu mindestens 80 % frei von Trägerteilchen ist.

3. Hydrierungskatalysator nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Oberfläche der Nickel/Nickelverbindung-Aggregate zu mindestens 90 % frei von Trägerteilchen ist.

4. Hydrierungskatalysator nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die durchschnittliche Teilchengröße der Nickel/Nickelverbindung-Aggregate im Bereich zwischen 5 und 25µm liegt.

5. Hydrierungskatalysator nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die durchschnittliche Größe der Nickelkristallite im Bereich zwischen 0,5 und 10 nm liegt.

6. Hydrierungskatalysator nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Größe der Nickelkristallite im Bereich von 1 bis 3 nm liegt.

7. Verfahren zur Herstellung eines auf Nickel basierenden Katalysators, enthaltend einen wasserunlöslichen Träger und gegebenenfalls einen Promotor, gemäß Anspruch 1, wobei eine Ausfällung von Nickelhydroxid/carbonat, eine Alterung, eine Abtrennung und eine Reduktion durchgeführt werden, gekennzeichnet durch mindestens 2 Stufen, nämlich

(I) eine rasche Fällungsstufe, bei der unter kräftigem Rühren das Nickelhydroxid/carbonat in einem Fällungsreaktor mit einer mittleren Verweilzeit von 0,01 bis 10 min, vorzugswelse 0,2 bis 4,5 min, ausgefällt wird, währenddessen die Normalität der Lösung in dem Reaktor, der einen Alkaliüberschuß enthält, zwischen 0,05 und 0,5 n, vorzugsweise zwischen 0,1 und 0,3 n, liegt und die Temperatur der Flüssigkeit in dem Fällungsreaktor zwischen 5 und 95 °C, vorzugsweise zwischen 20 und 55 °C, gehalten wird, sowie nachfolgend

(II) mindestens eine getrennte, längere Alterungsstufe mit einer mittleren Verweilzeit in dem Nachreaktor von 20 bis 180 min, vorzugsweisa zwischen 60 und 100 °C, insbesondere zwischen 90 und 98 °C, wonach der Feststoff abgetrennt, getrocknet und in an sich bekannter Weise mit Wasserstoff reduziert wird.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß die der Fällung zu unterwerfende Nickelsalzlösung 10 bis 80 g Nickel pro Liter enthält.

9. Verfahren nach Anspruch 7 oder 8, dadurch gekennzeichnet, daß der Träger in einer Menge von 20 bis 200 g pro Liter zugegeben wird.

10. Verfahren nach einem der Ansprüche 7 bis 9, dadurch gekennzeichnet, daß die Lösung der alkalischen Verbindung 30 bis 300 g einer wasserfreien alkalischen Verbindung pro Liter enthält.

11. Verfahren nach einem der Ansprüche 7 bis 10, dadurch gekennzeichnet, daß die alkalische Lösung Natriumcarbonat enthält.

12. Verfahren nach einem der Ansprüche 7 bis 11, dadurch gekennzeichnet, daß die Nickelverbindung ein Salz einer Mineralsäure ist.

13. Verfahren nach einem der Ansprüche 7 bis 12, dadurch gekennzeichnet, daß der Träger Siliciumdioxid ist.

14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß das eingesetzte Siliciumdioxid Kieselgur ist, welches zu 50 bis 90 Gew.% aus amorphem SiO_2 besteht.

15. Verfahren nach einem der Ansprüche 7 bis 14, dadurch gekennzeichnet, daß während der Fällung ein Rühren mit einer Zufuhr von mechanischer Energie von 5 bis 5000 kW, vorzugsweise 5 bis 25 kW, pro 1000 Liter der Lösung durchgeführt wird.

16. Verfahren nach einem der Ansprüche 7 bis 14, dadurch gekennzeichnet, daß das mechanische Rühren durch Strahlmischen bewirkt wird.

17. Verfahren nach einem der Ansprüche 7 bis 16, dadurch gekennzeichnet, daß das Aktivieren des

Katalysators mit Wasserstoff bei einer Temperatur zwischen 250 und 500 °C vorzugsweise zwischen 300 und 400 °C, durchgeführt wird.

18. Verfahren nach einem der Ansprüche 7 bis 17, dadurch gekennzeichnet, daß das Ausfällen kontinuierlich durch Eindosieren einer Trägersuspension in einer wäßrigen Nickelsalzlösung zusammen mit einer alkalischen Lösung in eine kleine, kräftig gerührte Mischpumpe und nachfolgendes Pumpen der Suspension in einen oder mehrere Nachreaktoren durchgeführt wird.

19. Verfahren nach Anspruch 18, dadurch gekennzeichnet, daß zwei oder mehr Nachreaktoren benutzt werden, wobei die Temperatur Im zweiten und jedem nachfolgenden Nachreaktor 5 bis 15 °C, unter der Temperatur im ersten Nachreaktor liegt.

20. Verwendung von Nickelkatalysatoren, wie in einem der vorstehenden Ansprüche beschrieben, zum Hydrieren von ungesättigten organischen Verbindungen.

Revendications:

1. Catalyseur d'hydrogénation, contenant de 10 à 90 parties en poids de nickel/composés de nickel et 90 à 10 parties en poids d'un vehicule insoluble dans l'eau et ayant une surface globale de nickel actif de 70-200 m^2/g, de préférence plus de 100 m^2/g de nickel, caractérisé en ce que le catalyseur comprend des agregats de nickel/composé de nickel d'une dimension moyenne de particules allant de 2 à 100 micromètres (µm) et en ce que la surface des agrégats de nickel/composé de nickel est au moins pour 60 % exempte de particules du vehicule.

2. Catalyseur d'hydrogénation selon la revendication 1, caractérisé en ce gue la surface des agrégats de nickel/composé de nickel est pour au moins 80 % exempte de particules du véhicule.

3. Catalyseur d'hydrogénation selon la revendication 1 ou 2, caractérisé en ce que la surface des agrégats de nickel/composé de nickel est pour au moins 90 % exempte de perticules du véhicule.

4. Catalyseur d'hydrogénation selon l'une quelconque des revendications 1 à 3, caractérisé en ce que la granulométrie moyenne des agrégats nickel/composé de nickel se situe entre 5 et 25 micrométres (µm).

5. Catalyseur d'hydrogénation selon l'une quelconque des revendications 1 à 4, caractérisé en ce que la dimension des cristallites de nickel se situe entre 0,5 et 10 nanomètres (nm).

6. Catalyseur d'hydrogénation selon l'une quelconque des revendications 1 à 5, caractérisé en ce que la dimension des cristallites de nickel se situe entre 1 et 3 nanomètres (nm).

7. Procédé pour la préparation d'un catalyseur à base de nickel comprenant un véhicule insoluble dans l'eau et facultativement un promoteur selon la revendication 1, procédé qui comprend la précipitation d'un hydroxyde/carbonate de nickel, le vieillissement, la séparation et la réduction, caractérisé en ce qu'il existe au moins deux stades à savoir (I) un stade de précipitation rapide, dans lequel, sous agitation vigoureuse, l'hydroxyde/carbonate de nickel est précipité dans un réacteur de précipitation avec une durée moyenne de séjour de 0,01 à 10, de préférence 0,2 à 4,5 minutes, pendant laquelle la normalité de la solution dans le réacteur, contenant un excès d'alcali, est entre 0,05 et 0,5, de preférence entre 0,1 et 0,3 N et la température du liquide dans le réacteur de précipitation est maintenue entre 5 et 95°C, de préférence entre 20 et 55°C suivi par (II) au moins un stade séparé, plus long, vieillissement, avec une durée moyenne de séjour dans le post-réacteur de 20 à 180 minutes, de façon préférée entre 60 et 100°C, de préférence entre 90 et 98°C, après quoi le solide est séparé, séché et réduit avec de l'hydrogène de façon connue.

8. Procédé selon la revendication 7, caractérisé en ce que la solution de sel de nickel à précipiter contient de 10 à 80 g de nickel par litre.

9. Procédé selon la revendication 7 ou 8, caractérisé en ce gu'on ajoute le véhicule en une proportion de 20 à 200 g par litre.

10. Procédé selon l'une quelconque des revendications 7 à 9, caractérisé en ce que la solution du composé alcalin contient de 30 à 300 g de composé alcalin anhydre par litre.

11. Procédé selon l'une quelconque des revendications 7 à 10, caractérisé en ce que la solution alcaline contient du carbonate de sodium.

12. Procédé selon l'une quelconque des revendications 7 à 11, caractérisé en ce que le composé de nickel est un sel d'un acide minéral.

13. Procédé selon l'une quelconque des revendications 7 à 12, caractérisé en ce que le véhicule est une silice.

14. Procédé selon la revendication 13, caractérisé en ce que la silice utilisée est le kieselguhr consistant en 50 à 90 % en poids de SiO_2 amorphe.

15. Procédé selon l'une quelconque des revendications 7 à 14, caractérisé en ce que pendant la précipitation, l'agitation a lieu avec une entrée de courant mécanique de 5 à 5000, de préférence 5 à 25 kwatts par 1000 litr s de solution.

16. Procédé selon l'une quelconque des revendications 7 à 14, caractérisé en ce que l'agitation mécanique est effectuée par mélange au jet.

17. Procédé selon l'une quelconque des revendications 7 à 16, caractérisé en ce gue l'activation du catalyseur est effectuée avec d l'hydrogène à une température entre 250 et 500, de préférence entre 300 et 400°C.

18. Procédé selon l'un quelconque des revendications 7 à 17, caractérisé en ce qu'on effectue la précipitation continuellem nt n dosant la suspension du véhi ule dans une solution agueus de sel de nickel ems mble avec une s lution alcaline dans une petite pompe mélangeuse entraînée vigoureusement en rotation et qui pompe

ensuite la suspension dans un ou plusieurs post-réacteurs.

19. Procédé selon la revendication 18, caractérisé en ce qu'on utilise deux ou plusieurs postréacteurs, la température dans le second et dans tout postréacteur suivant étant de 5 à 15°C plus faible que celle dans le premier post-réacteur.

20. Utilisation de catalyseurs de nickel comme décrit dans l'une quelconque des revendications précédentes, pour l'hydrogénation de composés organiques insaturés.

Fig. 1 Scanning electron micrograph of catalyst.
Magnification 1000x, green cake with Kieselguhr.

Fig. 2 Electron micrograph Guhr catalyst.
100 r.p.m., magnification 500x
(1mm $\simeq$ 2um).